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(54) **Photopolymer printing plates having a dimpled printing surface**

(57) A process for preparing photopolymer plates having a plurality of well-like depressions by exposing the photopolymer layer to actinic radiation through a photographic mask (30) containing optically transparent areas and optically opaque image areas, and a screen (10) having a plurality of opaque discrete dots (20) or other geometric shapes onto a photopolymer plate (40) and developing the plate, to form a plurality of depressions (51) in the relief planar surface of the exposed portions (50) of the photopolymer layer.

The application of printing ink to the relief printing surface causes the depressions on the relief surface to act as ink reservoirs resulting in the application of a more even distribution of ink to surfaces to be printed, particularly where large solid areas are printed.

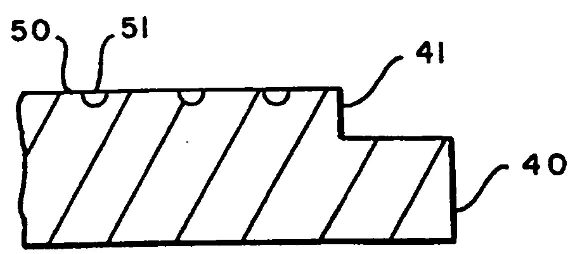

FIG. 3

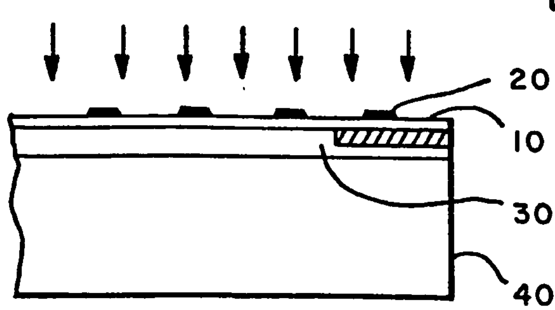

FIG. 2

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

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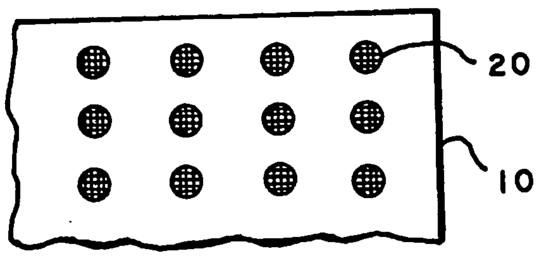

FIG.1

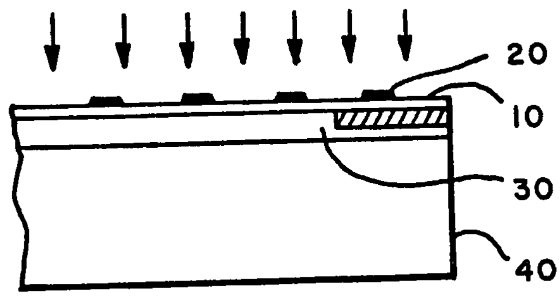

FIG.2

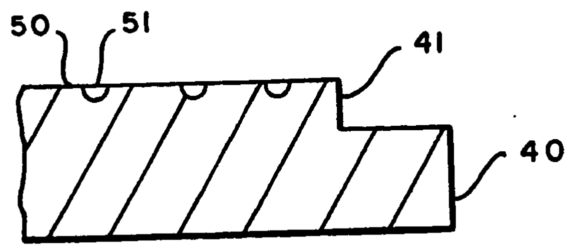

FIG.3

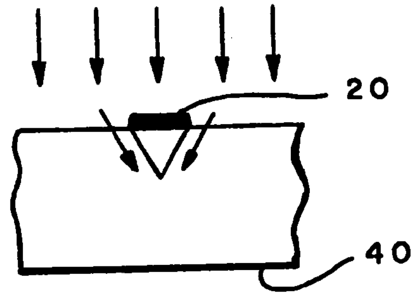

FIG.4

PHOTOPOLYMER PRINTING PLATES HAVING A DIMPLED PRINTING SURFACE

This invention relates to photopolymer printing plates having a printing surface of enhanced printing ink retention properties and to a process for producing such plates.

Flexography is a method to print onto flexible materials such as paper, plastic films and metal foils or to print irregular surfaced material such as corrugated board. In recent years photopolymer flexographic printing plates have become increasingly accepted in the industry because they are quicker and less costly to make than conventional molded rubber plates which are prepared by vulcanizing rubber in a mold under high temperature and pressure.

Photopolymer plates may be defined as sheets, films or laminates composed of a solvent soluble polymeric binder material and a photochemical system which undergoes polymerization or crosslinking when exposed to actinic radiation of the wavelength to which the photochemical system is sensitive. Thus, when such a system is exposed to light through a negative

transparent mask containing opaque image areas, the photochemical reaction on those areas of the surface of the plate which are exposed to light initiates a photopolymerization or crosslinking reaction, whereas those areas of the plate surface which are masked and not exposed to light remain essentially unchanged. The polymeric material in the exposed portion of the plate is thereby rendered less soluble or insoluble in solvent while the polymeric material in the non-exposed portions of the plate remains solvent soluble. A raised relief image may then be obtained by development of the plate to dissolve or wash away the soluble portions of the plate surface.

Polymer binder materials which are commonly employed in photopolymer printing plates include cross linkable polyamide binders such as disclosed in U.S. Patents 3,884,702 and 3,695,887. Elastomeric polymers are also used in such applications such as co-polymers of butadiene, particularly butadiene and acrylonitrile such as disclosed in U.S. Patents 4,177,074 and 4,415,649, polyurethanes such as disclosed in U.S. Patent 3,948,665, and block copolymers of butadiene or isoprene and a vinylaromatic monomer such as styrene, as disclosed in U.S. Patents 4,686,172 and 4,369,246.

Most of these systems are based on compositions containing a binder material, a diethylenically unsaturated monomer and a photoinitiator. These systems are all processed in a similar fashion which is to expose the presensitized elastomeric plate with ultraviolet light through a negative transparency. Addition polymerization occurs selectively in the exposed areas which corresponds to the clear areas of

the transparency, and substantially no polymerization occurs in unexposed areas which correspond to the opaque areas of the transparency. A relief image is produced when the plate is developed by brushing in a solvent. The system is designed so that the developing solvent dissolves the unexposed, unpolymerized areas and does not dissolve the exposed, polymerized areas.

Whereas flexographic plates prepared by exposing photopolymers to light are much easier to prepare than their molded vulcanized rubber counterparts, and offer the additional advantage that they can be exposed by computer laser, it is often more difficult to control the softness, flexibility and ink wetting properties of the printing surfaces of such plates. This can be a particular problem in those areas of the raised relief which contain printing characters having a relatively large printing surface area. In many applications, particularly flat bed printing, the printing ink tends to spread to the edges of large solid areas resulting in poor or uneven print density in the central regions of the printed character and diminishment of contrast along the edges of the printed character.

It is also known to employ photopolymer plates in planographic or lithographic printing processes. In such processes, the photopolymer layer on the plate is generally quite thin (not more than 0.015 mm thick) and the developed printing image is in the form of a series of half tone dots of varying sizes. Such plates are generally produced by forming a half tone image on a transparent mask by photographically exposing the mask to an original through a line screen, which mask is then subsequently used to expose the photopolymer plate

to produce a halftone dot image on the plate after development. Density of the solid printing surfaces on the printing plate may be controlled as a function of the dot size and dot density, or by etching the halftone dots to reduce their size. Examples of such techniques are disclosed in U.S. Patents 4,369,239 and 4,173,673. Since the printing surfaces of the plate are composed of a plurality of discrete half tone dots even in the denser printing areas, the printing of large surface areas is not as much of a problem as it is with flexographic processes, since the large printing surfaces are not composed of a contiguous mass of photopolymer, but rather a plurality of closely spaced, discrete dots.

The present invention provides a photopolymer printing plate for use in flexographic printing wherein the photopolymer relief structure is composed of printing characters of uniform printing height, the planar printing surfaces of which characters contain a plurality of well-like dimples or depressions present at a density within the range of from about 25 to about 500 depressions per linear inch of planar printing surface. The invention also provides a process for preparing such photopolymer plates by exposing the photopolymer layer to actinic radiation through a photographic mask containing optically transparent areas and optically opaque image areas, the transparent areas of said mask characterized by the presence of a plurality of opaque discrete dots or other geometric shapes present at a density of from about 25 to about 500 dots per linear inch. These dots serve to block a

portion of the light passing through the transparent areas of the mask thereby forming discrete regions in the underlying photopolymer layer which are not exposed or are only partially exposed. Upon development of the plate, the regions of the photopolymer layer underlying the dot pattern are removed resulting in the formation of a plurality of depressions in the relief planar surface of the exposed portions of the photopolymer layer.

Upon the application of printing ink to the relief printing surface of the plates of this invention, the depressions on the relief surface act as ink reservoirs resulting in the application of a more even distribution of ink to surfaces to be printed, particularly where large solid areas are printed.

The invention will be better understood from the following non-limiting description of an example thereof given with reference to the accompanying drawings in which:-

Fig. 1 is a vertical schematic (not to scale) view of a portion of a dot pattern present on a transparent base film or transparent areas of a negative mask film.

Fig. 2 is a side view of a laminate of the base film of Fig. 1 superimposed over a negative transparency, both of which are superimposed over a photopolymer layer.

Fig. 3 is a cross sectional side view of an exposed and developed photopolymer layer bearing well-like depressions on the raised printing surface.

Fig. 4 is a schematic diagram illustrating the methodology by which the well-like depressions on the printing surface shown in Fig. 3 are formed.

As indicated above, the photopolymer compositions which may be employed in the preparation of printing plates of this invention are known materials, and generally consist of at least about 30% by weight, more preferably at least about 70% by weight of a polymeric binder material and generally from about 1 to about 30% by weight of a photocrosslinkable monomer. Many of these compositions also contain an amount of photoinitiator sufficient to effect polymerization of the photocrosslinkable monomer when exposed to actinic radiation,said amount generally ranging from about 0.1 to about 10% by weight. The compositions may also contain fillers such as carbon black, silica or talc; dyes and pigments; plasticizers; polymerization inhibitors; and like additives.

The preferred binder materials for use in this invention include the elastomeric block copolymers of styrene and butadiene and the photochemical system as disclosed in U.S. Patents 4,369,246 and 4,686,172, the disclosures of which patents are incorporated herein by reference. Other systems include elastomeric binders based on copolymers of butadiene and a copolymerizable monomer such as acrylonitrile and the photochemical system such as disclosed in U.S. Patents 4,177,074 and 4,415,649; binders based on polyamides as disclosed in U.S. Patents 3,884,702 and 3,695,887; and binders based on polyurethanes as disclosed in U.S. Patent 3,946,665, the disclosures of each of which patents are incorporated herein by reference.

The photosensitive compositions are formulated as described in these patents and then calendared, or extruded, or cast from solvent into sheet material having a thickness in the range of from about 0.020 to about 0.250 inches. The sheet material is then cut to the desired dimensions prior to further processing steps. To convert inch distances into millimetres, multiply by 25.4.

Particularly preferred photopolymers are used in the form of a self supporting sheet and include dual layer photopolymer sheets marketed by DuPont under the trade name "CYREL PLS" (based on an ABA block copolymer of styrene and butadiene), elastomer sheets marketed by Uniroyal under the trade name "FLASKOR", and polyamide sheet material such as marketed by Toyobo under the trade name "PRINTIGHT UF" or by Toray under the trade name "TRORELIEF SS".

In accordance with the process of this invention, a photopolymer relief structure is prepared by exposing the photopolymer film or sheet to actinic radiation through a transparent mask containing an image negative having optically transparent areas and optically opaque image areas, a portion of the optically transparent areas on the film being blocked by a pattern of optically opaque discrete dots having a dot density of from about 25 to about 500 dots per linear inch. These dots serve to partially mask the transparent areas of the negative such that intermittent regions of the photopolymer underlying the dots are not exposed or only partially exposed to radiation while the surrounding regions of the photopolymer are exposed. Upon development of the photopolymer plate, non-exposed regions of photopolymer are removed resulting in an

imaged relief structure having relief or printing characters of uniform printing height wherein the printing surfaces of said characters contain a plurality of well-like depressions representing areas of the printing surface where unexposed photopolymer has been removed.

The series of opaque dots may be present on the negative transparency itself or may be provided by laminating a second transparent film screen containing the dots between the negative transparency and either the light source or the underlying photopolymer film, with the films arranged such that their surfaces are contiguous, i.e., in direct surface contact.

A transparency having the opaque dots directly on the photographic surface may be prepared at the time that the negative is prepared by the utilization of an appropriate contact screen or by computer controlled techniques wherein both the image and the pattern dots are created by computer controlled exposure using a laser beam. In such a case, a separate screen bearing the opaque dot pattern is not needed.

In the simpler embodiment, a separate transparent film bearing the opaque dot pattern is employed. Fig. 1 is a vertical schematic (not to scale) view of a corner of an optically transparent film material 10 having printed thereon a plurality of opaque dots 20. Suitable film materials include optically transparent cellulose acetate and oriented polyester having a preferred film thickness of less than 1 mil. The opaque dot pattern may be composed of silver halide photographic residue or the residue of a pigmented

photosensitive material. Alternatively, the dot pattern may be created on the film surface by printing or by electrophotographic techniques.

The dot pattern may be arranged in a linear array (as in Fig. 1), a rectilinear array or in a random array, with a dot frequency ranging from about 25 to about 500 dots per linear inch. In the more preferred embodiments, the dot frequency ranges from about 100 to about 400 per linear inch, with a frequency of from about 150 to about 300 per linear inch being most preferred. The screen dots generally all have about the same diameter which generally ranges from about 0.0005 to about 0.01 inches, with 0.0005 to about 0.002 inches being most preferred.

The term "dot" as used herein is intended to include not only circular geometry, but also other geometries as well such as diamond shapes, square shapes, oval shapes and the like, each of such size that they are essentially equivalent in surface area to circular dots having the diameters set forth above.

Fig. 2 shows a cross sectional view of a portion of the dot screen of Fig. 1 shown superimposed over negative transparency 30. The shaded area of transparency 30 represents a portion of an opaque image area present on the transparency whereas the non-shaded area represents a transparent area. Transparency 30 is in turn superimposed over photopolymer layer 40. The Figure also shows exposure of the structure to actinic radiation, depicted by vertical arrows.

Fig. 4 is a schematic illustrating the methodology by which the depressions in the planar printing surface of photopolymer layer 40 are formed. For clarity, screens 10 and 30 are not shown. Dot area 20 blocks the light which is directed perpendicularly upon the surface of the photopolymer layer, but diffuse components of the light represented by the converging arrows tends to expose regions of the photopolymer layer under the border of the dot circumference resulting in a graduated exposure in such regions. The triangular shape depicts the regions of unexposed photopolymer underlying an opaque dot after exposure of the photopolymer layer through the dot screen.

Fig. 3 is a cross sectional illustration of photopolymer layer 40 after development. The edge of the relief structure character is shown by wall 41. Planar printing surface 50 contains a plurality of well like and ink retaining depressions 51 which are generated as a consequence of development of the exposed photopolymer layer.

The depth and width of the well-like depressions in the printing surface shown at 51 in Fig. 3 may be controlled largely as a function of the size of the masking dot, the intensity of the exposure source, and the degree to which the masking dots are opaque to the exposure light. Generally speaking, dot depths of from about 0.0005 to about 0.005 inches are preferred for the purposes of this invention, with the most preferred depths ranging from about 0.001 to about 0.003 inches.

Actinic radiation from any source and of any type can be used in the process. The radiation may emanate from

point sources or be in the form of parallel rays or divergent beams. By using a broad radiation source, relatively close to the image-bearing transparency, the radiation passing through the clear areas of the transparency enters as divergent beams and thus irradiates a continually diverging area in the photopolymerizable layer underneath the clear portions of the transparency, resulting in a polymeric relief having its greatest width at the bottom of the photopolymerized layer, i.e., a frustum, the top surface of the relief being the dimensions of the clear area. Inasmuch as the free-radical-generating addition-polymerization initiators activatable by actinic radiation generally exhibit their maximum sensitivity in the ultraviolet range, the radiation source should furnish an effective amount of this radiation. Such sources include carbon arcs, mercury-vapor lamps, fluorescent lamps with special ultraviolet-light-emitting phosphors, argon glow lamps, and photographic flood lamps. Of these, the mercury-vapor lamps, particularly the sunlamp or "black light" type, and the fluorescent sunlamps are most suitable.

The solvent liquid used for washing or developing the photosensitive plates should have good solvent action on the solvent-soluble portions of the exposed photopolymer plate and little or no action on the photopolymerized portions of the plate. Suitable solvents include water or aqueous solutions of a base such as an alkali metal hydroxide or an alkali metal meta silicate for use with those photopolymers which are developable by aqueous solutions. Plates based on elastomeric polymer binders may be developed using

organic solvents such as methyl ethyl ketone, benzene, toluene, trichloroethane, perchloroethylene and similar materials.

The printing reliefs made in accordance with this invention can be used in all classes of printing but are most applicable to those classes of printing wherein a distinct difference of height between printing and non-printing areas is required and particularly to the flexographic printing class wherein a resilient print area is required, e.g., for printing on deformable printing surface. These classes include those wherein the ink is carried by the raised portion of the relief such as in dry-offset printing, ordinary letterpress printing, the latter requiring greater height differences between the printing and nonprinting areas. The height of the relief characters preferably ranges from about 0.01 to about 0.05 inches.

Inks which may be used in conjunction with the printing plates of this invention may be aqueous based or solvent based. Preferred inks for plates developed with organic solvent are glycol based inks and preferred inks for plates developed with aqueous based solvents are ester based inks, such as di-octyl phthalate, and preferably contain fluorescent dyes or pigments and a small amount of surfactant.

The following Examples are illustrative of the invention.

Example 1

An 11 inch by 8.5 inch sheet of elastomeric photopolymer supplied by DuPont under the trade name CYREL PLS which is based on a block ABA copolymer of styrene and isoprene and containing a diethylenically unsaturated monomer and a photoinitiator was provided. The sheet had a thickness of 0.067 inch.

A relief image on the surface of the photopolymer sheet was prepared by first blanket exposing to actinic radiation the side of the sheet opposite the side to bear the relief image for 30 seconds using an exposure unit supplied by Greig Machine, Inc., Model 48. The UV energy level was from about 4-6 milliwatts/cm^2. This initial reverse side exposure initiates photopolymerization which controls the depth of the relief image to be obtained on the opposite side of the sheet. The sheet was next turned over and exposed to UV light through a negative transparency bearing postage meter indicia having superimposed thereover a transparent sheet having on its surface a plurality of linear opaque dots having a frequency of about 167 dots per linear inch. The exposure conditions were 25 minutes at 4-6 milliwatts/cm^2.

The plate was then developed by brushing the image-exposed surface in a solvent comprising a mixture of perchlorethylene and 25% by weight N-butanol for a period of about 7 minutes. The plate was then heated to about 70°C for about 60 minutes to remove the solvent, followed by a 16 minute post exposure to actinic light to cure and detackify the plate.

The resulting plate had an indicia relief depth of about 0.025 inch.

The postage meter relief image was cut from the sheet and mounted on a Pitney Bowes B-2 postage meter. The relief surface was inked using a glycol based red ink. Flexographic print quality of the image on white paper was excellent.

Examples 2-6

Five additional photopolymer sheets were exposed, developed and tested for print quality. Process parameters were the same as in Example 1 except that in the case of Examples 4, 5, and 6, the back exposure time was 1.75 minutes, the image exposure time was 3 minutes, development time was 3.5 minutes, drying time was 25 minutes post curing time was 5 minutes, and the developer was an aqueous alkali solution. The materials and screen dot density are shown in Table 1.

A control plate was also prepared using the materials and the process of Example 1, except that the transparent sheet bearing the opaque dot pattern was not used in the image exposure step. Print results using this plate are also shown in Table 1.

As is evident from this data, the print quality in solid areas of the print is notably superior when printing is conducted using the photopolymer plates made in accordance with this invention.

TABLE 1

Photo-polymer	Plate Thickness	Dots Per Inch	Ink Base	Print Quality	Relief Depth
Ex1 - DuPont PLS	0.067"	167	Glycol	Excellent	0.025"
Ex2 - DuPont PLS	0.045"	255	Glycol	Excellent	0.035"
Ex3 - Uniroyal Flaskor	0.067"	255	Glycol	Excellent	0.030"
Ex4 - Toyobo Printight	0.048"	255	Diester	Excellent	0.030"
Ex5 - Toray Trorelief 95SS	0.038"	255	Diester	Excellent	0.025"
Ex6 - Toray Trorelief 95SS	0.038"	167	Diester	Excellent	0.025"
Control	0.067"	167	Glycol	Poor	0.030"

A print quality of excellent means that areas printed on paper and having a solid print dimension of greater than about 1/16 inch exhibit substantially uniform print density throughout the printed area. A print quality of poor means that the same printed areas show numerous white spots representing void areas and areas of low print density where the paper shows through, indicative of non-uniform ink application in those areas.

CLAIMS

1. A photopolymer relief structure for use in flexographic printing having printing characters of uniform printing height, the planar printing surfaces of which characters contain a plurality of well-like depressions present at a density of from about 25 to about 500 depressions per linear inch of planar printing surface.

2. The relief structure of Claim 1 wherein said depressions range from about 0.0005 to about 0.005 inch in depth in said planar printing surface.

3. The relief structure of Claim 2 wherein said depressions range from about 0.001 to about 0.003 inch in depth in said planar printing surface.

4. The relief structure of claim 1,2 or 3 wherein the density of said depressions ranges from about 100 to about 400 per linear inch of planar printing surface.

5. The relief structure of claim 1,2,3 or 4 wherein the diameter of said depressions ranges from about 0.0005 to about 0.01 inch.

6. The relief structure of Claim 5 wherein the diameter of said depressions ranges from about 0.0005 to about 0.002 inch.

7. A process for forming a photopolymer relief structure having a dimpled printing surface for use in flexographic printing comprising:

(a) providing a film of positive acting photopolymer composition;

(b) laminating said photopolymer film with an image mask film containing optically transparent areas and optically opaque areas such that the surface of said mask film is contiguous with the surface of said photopolymer film;

(c) optionally laminating to said mask film or between said mask film and said photopolymer film a second film containing optically transparent areas such that the surfaces of said films are contiguous, the transparent areas on at least one of said mask film or said second film characterized by the presence of a plurality of optically opaque discrete dots present on the film surface at a density of from about 25 to about 500 dots per linear inch,

(d) exposing said photopolymer film to actinic radiation through said mask film and said optional screen film; and

(e) removing said mask film and said optional screen film from the surface of said photopolymer film; and

(f) developing said photopolymer film by contact with a solvent which removes the unexposed areas of said photopolymer film.

8. The process of Claim 7 wherein said dots are present at a density of from about 100 to 400 per linear inch.

9. The process of Claim 7 wherein said dots have a diameter ranging from about 0.0005 to about 0.01 inch.

10. The process of Claim 9 wherein said dots are substantially equal in surface area and have a diameter ranging from about 0.0005 to 0.002 inch.

11. The process of Claim 7 wherein said photopolymer layer is exposed such that the dimples on said printing surface after development have a depth ranging from about 0.0005 to abut 0.005 inch.

12. The process of Claim 7 wherein the second film containing a plurality of optically opaque discrete dots on the screen surface is present in the laminate.

13. The process of Claim 12 wherein said second film is in contiguous contact with said image mask film and is positioned between said image mask film and said exposure source.

14. A photopolymer relief structure substantially as herein described with reference to and as illustrated in the accompanying drawings.

15. A process for forming a photopolymer relief structure substantially as herein described with reference to and as illustrated in the accompanying drawings.

16. Any novel combination or sub-combination of features disclosed and/or illustrated herein.

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